

Advantages of blending $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ into $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ cathodes

Tatsuji Numata^{a,*}, Chika Amemiya^b, Tomokazu Kumeuchi^a,
Masato Shirakata^a, Masatomo Yonezawa^a

^aNEC Corporation, Functional Devices and Materials Research, 1-1, Miyazaki 4-Chome, Miyamae-ku, Kawasaki, Kanagawa 216-8555, Japan

^bNEC, NEC Electron Devices, Electronic Component Operations Unit, 1-1, Miyazaki 4-Chome, Miyamae-ku, Kawasaki, Kanagawa 216-8555, Japan

Received 11 July 2000; received in revised form 8 February 2001; accepted 13 February 2001

Abstract

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ blending was investigated as a way to overcome the problems associated with lithium ion rechargeable batteries that use manganese spinel as a cathode material. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is a useful additive for preventing HF-generation and Li-loss in electrolytes during storage at elevated temperatures. In experiments, the Mn dissolution from the spinel structure into the electrolyte was decreased by adding $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. This dissolution was almost completely eliminated by 15 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ blending. As a result, this blending technique can prevent the decline in capacity caused by storage at elevated temperatures. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Manganese spinel; $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$; Mn dissolution; Blended cathode; Storage; Recovery capacity

1. Introduction

Spinel-type lithium manganese oxide, LiMn_2O_4 , is one of the most promising cathode materials for lithium ion rechargeable batteries [1,2]. It has a very safe crystal structure, and it also has cost and environmental advantages. In addition, LiMn_2O_4 is expected to offer high power density [3,4], so it has been the subject of great interest for use in large cells, particularly for those use in electric vehicles. Despite these advantages, cycle and storage performance of cells using LiMn_2O_4 degrades at elevated temperatures. Mn dissolution from the spinel structure is one of the causes of this cycle fade [5]. Pasquier et al. demonstrated that capacity loss in LiMn_2O_4 -based Li cells is associated with Mn dissolution and protonated $\lambda\text{-Mn}_2\text{-yO}_4$ [6].

We have investigated the Mn dissolution that occurs when powder is stored in electrolyte. Some consider Mn dissolution to be a relative minor problem, while it is not the sole cause of cycle fade, improvements will certainly increase storage performance. Additives that consume water or prevent acid-generation may solve those problems because Mn dissolution seems to increase when acid is present in the electrolyte.

LiNiO_2 is also suitable for use in lithium ion rechargeable batteries because it has high capacity. However, LiNiO_2 cells

seldom pass over-charge or hot-box tests. Slurry gelling caused by basicity adds to the problems associated with using LiNiO_2 , by itself, as the cathode material.

Focusing on basicity, LiNiO_2 -based material blended with LiMn_2O_4 was investigated as an additive for preventing Mn dissolution. HF and Mn ion concentrations in electrolytes were analyzed in cathodes with various blends of LiNiO_2 -based material. This LiNiO_2 -based material proved effective in preventing Mn dissolution. As a result, lithium ion cells with blended cathodes showed excellent recovery capacities even after high temperature storage.

2. Experimental

Manganese spinel, $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ powders were synthesized by solid state reaction [7]. Lithium carbonate was pulverized, and electrolytic manganese dioxide (EMD) was classified into appropriate particle size distributions for immediate reactions and desired particle sizes. These raw materials were mixed well and calcinated with two consecutive heat treatments at 600–870 °C with intermediate grinding.

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was selected as an additive because it is easier to handle and cycles more stable than stoichiometric LiNiO_2 . The specific surface area was measured by using Quanta Chrome Quanta Sorb with N_2 adsorption.

The storage tests were done in the following way. The blended manganese spinel and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was put into a

* Corresponding author. Tel.: +81-44-856-8495; fax: +81-44-856-8079.
E-mail address: t-numata@ah.jp.nec.com (T. Numata).

Ni-plated Fe 18,650 cans along with 5 cm³ of electrolyte. Then, the 18,650 cans were sealed by crimping and stored for 10 days in an incubator at 80°C. After storage, the Mn dissolution and the Li and HF concentrations were measured by inductively coupled plasma spectrometry (ICP), atomic adsorption and ion chromatography. The powders were analyzed by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared spectrometer (FT-IR). The TGA measurements were done using Perkin-Elmer TGA7 equipment in a dry air atmosphere. The FT-IR measurements were carried out using Bio-Rad FTS-40A.

The electrochemical properties were evaluated by using coin and cylindrical cells. The coin cells had 1.4 mm thick Li metal foil anodes and microporous polypropylene separators. The composite cathodes were made from active material (92.0 wt.%), carbon black (5.0 wt.%) and polyvinylidene fluoride (PVDF) binder, uniformly coated on aluminum foil. The cathode powder and carbon black were added to a solution of 6% PVDF in *N*-2-methyl pyrrolidone (NMP) so that 3.0% of the final electrode mass would be PVDF. The slurry was coated on the Al foil, and the NMP was evaporated by heating. Test electrodes were 12 mm Ø in diameter with thickness about 100–200 µm. The electrolyte used in the cells was 1 M LiPF₆ dissolved in EC/DEC (30/70, v/v). The cell construction and sealing were done in a dry room (dew point \approx –60°C), and the construction used 2320 coin hardware. The charge/discharge tests were performed at a constant current, with voltage ranging between 3.0 and 4.3 V.

We fabricated the 18,650 cylindrical cells with identical cathode, separator and electrolyte specifications. The anodes consisted of graphite (90.0 wt.%), carbon black (1.0 wt.%) and PVDF binder (9.0 wt.%), uniformly coated on copper foil. The anodes were about 100–150 µm thick. Cell construction and crimping were also done in a dry room. The cycling current was 1 C, and the cycling tests were carried out at voltage ranging between 3.0 and 4.2 V. The recovery capacities after storage were also measured.

3. Results and discussion

The HF and Li concentrations in the electrolyte after storage are shown in Fig. 1. The electrolyte originally had 20 ppm HF, and after 10 days of storage, there was no change at either room temperature or 80°C. However, with manganese spinel, HF concentration increased to 260 ppm, and the Li concentration decreased by about 20% (Li concentration in the initial state was 5800–6000 ppm). The HF generation was not induced by water trapped in the powder; the LiNi_{0.8}Co_{0.2}O₂ had seven times more humidity than the manganese spinel. As previously reported [6,8–10], water is generated due to the co-existing of manganese oxide. By contrast, LiNi_{0.8}Co_{0.2}O₂ obviously had an impact on the HF and Li concentrations after high temperature soaking. The electrolyte maintained its original

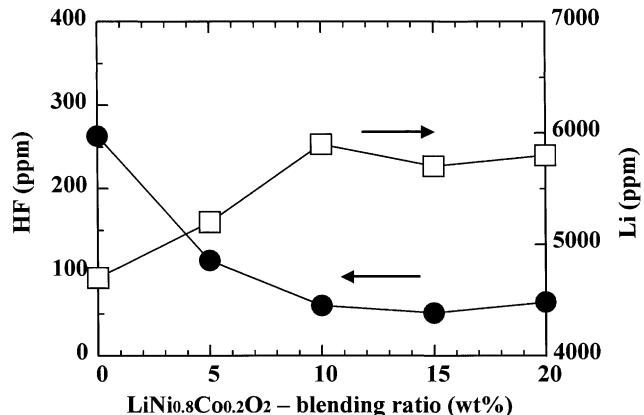


Fig. 1. HF and Li concentrations in electrolyte after storage at 80°C for 10 days. The electrolyte was 1 M LiPF₆ dissolved in EC/DEC.

compositions of Li and HF when blended with LiNi_{0.8}Co_{0.2}O₂ of more than 10 wt.%.

LiNi_{0.8}Co_{0.2}O₂ also served as an agent for avoiding Mn dissolution from the spinel structure. Fig. 2 shows the Mn concentrations after storage tests with various LiNi_{0.8}Co_{0.2}O₂ blending ratios. Mn dissolution decreased as the content of LiNi_{0.8}Co_{0.2}O₂ increased. It was almost completely eliminated when the cathode was blended with LiNi_{0.8}Co_{0.2}O₂ of more than 15 wt.%. Moreover, the B.E.T. surface area of LiNi_{0.8}Co_{0.2}O₂ drastically affected Mn dissolution. This seems to explain the exchange reaction between the H⁺ and Li⁺ in the LiNi_{0.8}Co_{0.2}O₂. Based on the assumption that 10 wt.% blending is sufficient when the surface area of LiNi_{0.8}Co_{0.2}O₂ is greater than 0.76 m²/g (Fig. 2), we used these values in our experiments.

Fig. 3 shows the TGA curves of the cathode powder before and after storage. There was a significant change in the TGA curve of manganese spinel after high-temperature soaking (Fig. 3a). The curve after soaking showed a

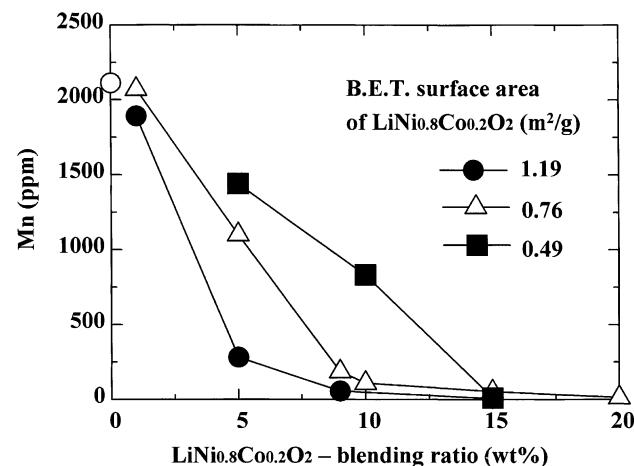


Fig. 2. Mn dissolution from spinel structure into electrolyte after storage test with various LiNi_{0.8}Co_{0.2}O₂ blending ratios. The amount of Mn dissolution was also affected by the surface area of LiNi_{0.8}Co_{0.2}O₂.

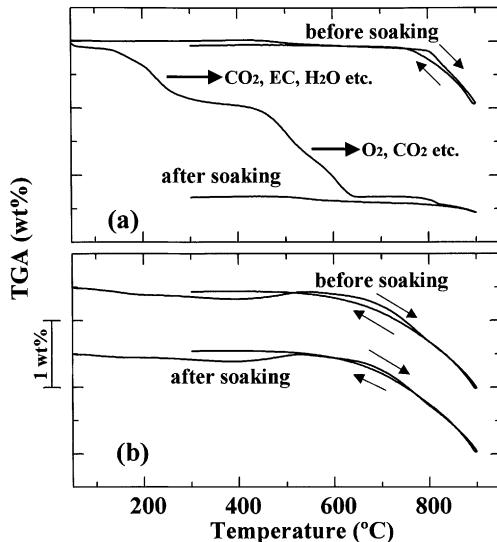


Fig. 3. TGA curves of cathode powder before and after storage: (a) without $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ blending; (b) manganese spinel + $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ = 90 + 10 (wt.%). The gas compositions were detected by TG-MAS.

weight loss of approximately 2 wt.% at temperatures below 600°C. Based on these results, we conclude that the weight loss was caused by organic compounds which may have been deposited on cathode powder. By contrast, the blended cathode showed identical TGA curves before and after soaking (Fig. 3b). Similar results were observed in the FT-IR spectra of the powder surface. There was no change in the IR spectra of the blended cathode after soaking. The IR spectrum of manganese spinel without $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ after soaking, however, suggests CH_2 , $\text{C}=\text{O}$ and $\text{C}-\text{O}$ absorption. We conclude that $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ blending suppresses electrolyte decomposition.

We can see that $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ blending has a big impact on storage performance. The ratios of the recovery capacities to the initial capacities of the 18,650 cells stored for 4 weeks at 60°C, are shown in Fig. 4. The cells with blended cathodes maintained higher capacities than those without $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ blending. Storage performance was improved by using a blended cathode.

The mechanism responsible for this increased storage performance is not completely clear. However, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ blending clearly prevents Mn dissolution and electrolyte decomposition. The crucial factor is that no water is generated when the acid is consumed. The exchange reaction between H^+ and Li^+ in $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is the most reasonable.

In addition, because the charge–discharge performance of a blended cathode can be represented as a composite of the properties of each material, it has one other advantage. The

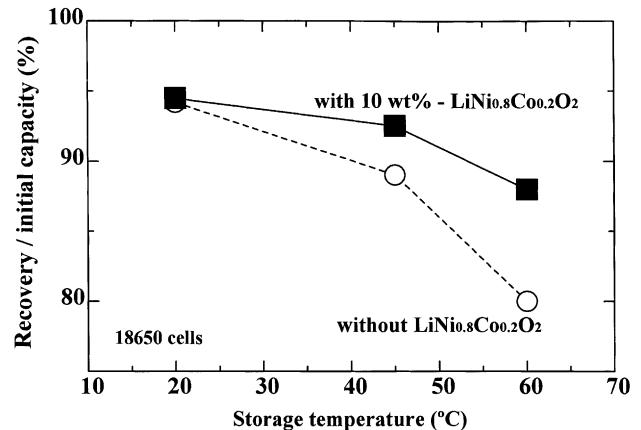


Fig. 4. Recovery capacity/initial capacity (%) of 18,650 cylindrical cells with graphite anode, after 4 weeks storage at 60°C, DOD = 0%.

cell capacity of a blended cathode in the range between 3.0 and 4.3 V can be improved by increasing $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ content [11,12].

4. Summary

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was investigated as an additive for consuming HF in electrolytes. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ serves as an agent, thus avoiding HF-generation and Li-loss after storage at elevated temperatures. Blending $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ with manganese spinel was found to prevent Mn dissolution from the spinel structure. Mn dissolution can be almost completely eliminated by 15 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ blending. Consequently, recovery capacity after high-temperature storage was improved.

References

- [1] T. Numata, et al., in: Proceedings of the 190th Meeting of the Electrochemical Society, San Antonio 1996, p. 1014.
- [2] Y. Shimakawa, et al., J. Solid State Chem. 131 (1997) 138.
- [3] A.M. Wilson, et al., in: Proceedings of the 39th Battery Symposium, Japan, 1998, p. 23.
- [4] T. Ohta, et al., in: Proceedings of the 196th ECS Fall Meeting Abstracts, Hawaii, Vol. 99-2, No. 95, 1999.
- [5] A. Bylr, et al., J. Electrochem. Soc. 145 (1) (1998) 194.
- [6] A.D. Pasquier, et al., J. Electrochem. Soc. 146 (2) (1999) 428.
- [7] T. Numata, et al., NEC Res. Dev. 38 (3) (1997) 294.
- [8] Y. Wang, et al., in: Proceedings of the 9th International Meeting on Lithium Batteries, Poster 3, 1996.
- [9] J.N. Reimers, et al., in: Proceedings of the 196th ECS Fall Meeting Abstracts, Hawaii, Vol. 99-2, No. 140, 1999.
- [10] E. Wang, et al., J. Electrochem. Soc. 147 (11) (2000) 4023.
- [11] T. Kumeuchi, et al., ITE Battery Lett. 2 (2001) 41–47.
- [12] T. Numata, et al., NEC Res. Dev. 41 (1) (2000) 8.